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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C08G 59/06, 59/32, 81/00		A1	(11) International Publication Number: WO 87/02043 (43) International Publication Date: 9 April 1987 (09.04.87)
(21) International Application Number: PCT/US86/02035			(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent), US.
(22) International Filing Date: 29 September 1986 (29.09.86)			
(31) Priority Application Number: 4200/85-2			
(32) Priority Date: 27 September 1985 (27.09.85)			
(33) Priority Country: CH			Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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(54) Title: EPOXY RESIN POWDER COATING COMPOSITION

(57) Abstract

The powder coating composition contains a solid epoxy resin which has an average epoxide functionality per molecule of greater than 2 and a solid curing agent for the epoxy resin. The solid epoxy resin is multifunctional polyglycidyl ether of a bisphenol compound or a multifunctional polyglycidyl ether of a polyglycol advanced in molecular weight with bisphenol compounds. The coating compositions are particularly useful for coating metallic substrates.

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Epoxy Resin Powder Coating Composition

The present invention relates to a powder coating composition containing a solid, multi-functional epoxy resin, a process for coating a substrate with the powder coating composition and to a coated substrate.

5

Epoxy resins have been known for a long time. For example, from US Patent 4 251 594, epoxy resins 10 prepared by reacting a glycidyl ether of a dihydric phenol with a dihydric phenolic compound are known. These resins are used as liquids or dissolved in a 15 solvent for impregnating substrates for use in preparing electrical laminates.

Epoxy resin powder coating compositions are 20 capable of being cross-linked by a variety of different cross-linking agents. The epoxy resins used for this purpose are mainly poly epoxides of the 25 epichlorohydrin/bisphenol A type with, on the average, one to less than two 1,2-epoxy groups per molecule. Suitable curing agents are well known in

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the art. Examples are amines, acid anhydrides, boron trifluoride complexes, dicyandiamide, substituted dicyandiamides, phenolic resins as well as polyester 5 resins. However, the cured coatings prepared from these epoxy resins do not possess the properties, such as impact resistance or solvent resistance, required for many applications.

10

One method for improving the chemical and physical properties of such coating composition consists of adding a polyfunctional epoxy resin, such as 15 an epoxy novolac resin, to the epichlorohydrin/- bisphenol A type resin. Epoxy novolac resins, which are commonly the reaction product of epichlorohydrin 20 with the reaction product of a phenol and formaldehyde are conventionally prepared at an average epoxide functionality of from 2.2 to 8 epoxy groups 25 per molecule. However, these polyfunctional epoxy compounds are relatively expensive. In addition, the reactivities of the epoxy groups of the epoxy novolac 30 resins or other polyfunctional epoxy resins are often different from reactivities of the epoxy groups of more conventional epichlorohydrin/bisphenol A type 35 resins. These differences in reactivity of the epoxy groups can cause embrittlement or other problems upon curing a blend containing the two resin types. Moreover, since the epoxy novolac resins presently 40 used are liquid or semi-solid and the epichlorohydrin/bisphenol A type resins are solid under standard conditions (i.e., 20°C and 1 bar air pressure) these resins must be blended as a molten

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mass. This process is costly and time consuming and the semi-solid epoxy novolac resins are difficult to handle. Therefore, it would be highly desirable to 5 prepare a powder composition for coating a substrate which composition does not have the above mentioned disadvantages.

10 Accordingly, one aspect of the present invention is such a powder coating composition containing a solid, multifunctional epoxy resin having an average 15 epoxide functionality per molecule of greater than two. More specifically, one aspect of the present invention is a powder coating composition which comprises a solid, epoxy resin and a solid curing 20 agent for the epoxy resin characterized in that the solid epoxy resin is a solid, multifunctional polyglycidyl ether of a bisphenol compound or a solid 25 multifunctional polyglycidyl ether of a polyglycol advanced in molecular weight with a bisphenol compound represented by formula I below or a mixture 30 thereof. The powder coating composition can comprise optional additives, for example accelerators, flow control agents, pigments and/or fillers. The powder compositions are used for coating a substrate, preferably 35 a metal, glass, plastic or fiber reinforced plastic substrate.

40 One advantage of the powder compositions of the present invention is the short gel time compared to known compositions containing polyglycidyl ethers of bisphenol compounds or of polyglycols with an average

epoxide functionality per molecule of two or less. Moreover, the cured coatings provided by the powder compositions of the present invention usually have good chemical and physical properties like high impact resistance, high solvent resistance, high flexibility and/or low brittleness. The powder compositions of the present invention do not require special processing or application equipment for applying the compositions to the substrate.

Another aspect of the present invention is a process for preparing a composition of the present invention by blending the above mentioned solid, multifunctional epoxy resin(s), the solid curing agent(s) and optionally further additives, passing the mixture through an extruder and grinding the extrudate.

A further aspect of the present invention is the use of a powder coating composition of the present invention for coating a substrate. Preferably, the substrate is coated by electrostatic spraying or by using a fluidized bed which can also be electrostatic.

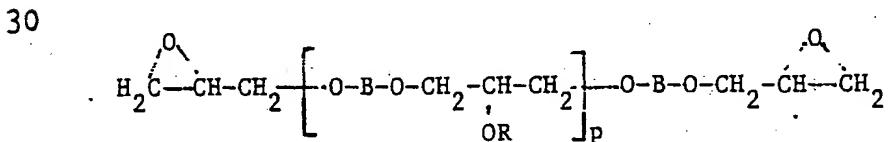
The present invention also relates to a substrate having a coating on at least one surface thereof, which coating consists essentially of the powder composition as described herein, after being cured.

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As used herein "multifunctional" epoxy resins refer to resins with an epoxide functionality per molecule of greater than two, meaning that the 5 average number of 1,2-epoxy groups per resin molecule is greater than 2.

10 The "epoxy equivalent weight (EEW)" is the weight of the epoxy resin containing one equivalent of epoxy groups. It is measured by two standard titration methods.

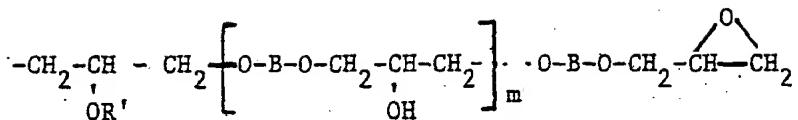
15 The multifunctional epoxy resins, i.e., the multifunctional polyglycidyl ethers of bisphenol 20 compounds and the multifunctional polyglycidyl ethers of polyglycols advanced in molecular weight with bisphenol compounds, are solids at room temperature and 1 bar air pressure. The above mentioned 25 multifunctional polyglycidyl ethers of bisphenol compounds and of polyglycols are represented by the following formula:



(I);

40 wherein R is independently, each occurrence, hydrogen or a radical of the formula II

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5

(II);

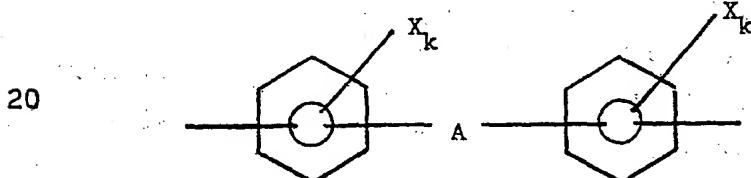
R' has the meaning of R;

10

each B is independently an aliphatic alkyl radical or a polyglycol radical of a number average molecular weight from 100 to 4000, preferably from 300 to 2000

15

or a radical of the formula



(VII);

provided that at least a part of the radicals B are
30 radicals of VII;each A is independently, each occurrence, a divalent hydrocarbon group having from 1 to 8 carbon atoms,
35 -CO-, -O-, -S-, -S-S-, -S(O)₂-, -S(O)-, or a covalent bond;X is independently, each occurrence, hydrogen,
40 halogen or an alkyl group of 1 to 4 carbon atoms;

p has an average value of greater than 0 and up to 20, preferably of greater than 0 and up to 10; m has

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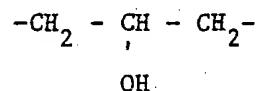
an average value of 0 up to 20, preferably of 0 up to 10; and k is a positive number from 1 to 4; provided that the average epoxide functionality per molecule of the epoxy resin is greater than 2 and the epoxy resin is a solid.

Preferably, the average values of each of p and 10. m are larger than 0.25, most preferably, larger than 0.5.

As stated above, each R is, in each occurrence, 15 independently hydrogen or a radical of the formula II, provided that the average epoxide functionality per molecule of the epoxy resin is greater than 2. 20 Therefore, at least some of the radicals R are not hydrogen.

In formula II, R' represents hydrogen or the 25 radical of formula II. This means that the individual branch(es) of the epoxy resin of formula I can themselves be branched.

30 The hydrogen atom of the hydroxy moiety in the group



35

40 in formula II can in principle also be substituted by a radical of formula II.

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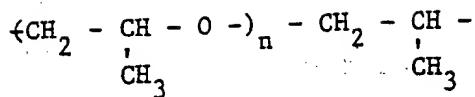
The numerical values of p and m and the meaning of R and R' are chosen so that the average epoxide functionality per molecule is greater than 2 and the 5 resin is a solid.

The multifunctional polyglycidyl ethers of 10 bisphenol compounds and the multifunctional polyglycidyl ethers of polyglycols advanced in molecular weight with bisphenol compounds, i.e., the compounds of the formula I, have preferably an 15 average epoxide functionality per molecule of at least 2.1, more preferably at least 2.3 and have preferably an average epoxide functionality per 20 molecule of at most 5.0, more preferably, at most 3.5.

The epoxy resin can have any epoxy equivalent 25 weight provided that the epoxy resin is solid prior to curing. Preferably, the epoxy equivalent weight of the described epoxy resins is greater than about 30 300, more preferably greater than about 500; and preferably less than about 2000, more preferably less than about 1200.

35 Preferred examples of multifunctional polyglycidyl ethers of polyglycols of formula I advanced in molecular weight with bisphenol com- 40 pounds, are those wherein a part of the radicals B are a polyalkylene glycol radical, e.g., a poly- propylene glycol radical represented by the formula

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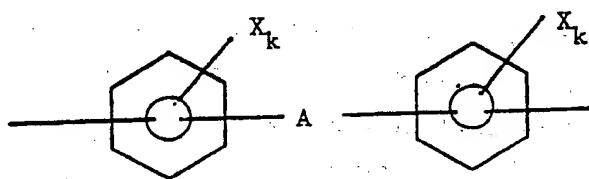
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10 wherein n is from 1 to 35, preferably from 1 to 20.

15 The epoxy resins which are preferred for the use
 20 of the present invention are those represented by
 formula I in which at least a part of the radicals B
 25 have a meaning of

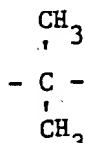
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25



30 wherein A represents independently, each occurrence,
 a divalent hydrocarbon group having from 1 to 6
 35 carbon atoms, most preferably a 2-propylidene
 radical, i.e., the radical presented by

40



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X is independently, each occurrence, hydrogen, bromine or chlorine; and k is as defined hereinbefore.

5

Preferably, the powder coating compositions of the present invention comprise the multifunctional polyglycidyl ethers of bisphenol compounds and/or the multifunctional polyglycidyl ethers of polyglycols advanced in molecular weight with bisphenol compounds in amounts of from about 10 percent, more preferably 10 from about 20 percent to about 95 percent, more 15 preferably to about 70 percent, by weight of the composition.

20

The epoxy resin component of the powder coating composition of the present invention can be prepared by branching the corresponding linear diglycidyl 25 ethers of bisphenol compounds or the corresponding linear polyglycidyl ethers of polyglycols, e.g., as described in US Patents 4,352,918 and 4,251,594.

30

The branching reaction, however, occurs preferably in the presence of an alkali compound, most preferably in the presence of a lithium or 35 cesium compound.

Preferably, the method of preparing the epoxy 40 resin component of the powder coating composition of the present invention comprises "advancing" an epoxy resin such as a diglycidyl ether of a bisphenol, of a diol or of a polyglycol of low molecular weight with

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a polyol such as, for example, with a bisphenol, in the presence of an "advancement" catalyst to prepare a higher molecular weight epoxy resin and, thereafter, branching the epoxy resin in situ using a lithium or cesium compound as the branching catalyst. Alternatively, the branching reaction may occur simultaneously with the advancement of the epoxy resin.

Advancement catalysts are well known in the art. Illustrative advancement catalysts which form higher molecular weight linear epoxy resins include the "onium" compounds such as quarternary ammonium compounds. Examples are quarternary ammonium hydroxides, as described in U.S. Patent 4,168,331, e.g., tetramethylammonium hydroxide; quarternary ammonium salts and quarternary phosphonium salts, such as ethyltriphenylphosphonium iodide; and the tertiary amines and phosphines, e.g., benzylidemethylamine and triphenylphosphine. Of the advancement catalysts, the onium compounds and the tertiary amines are generally more advantageously employed. Advantageously, the advancement catalysts will be employed at about 150 to 2500 parts per million (ppm), by weight, based on the total weight parts of the epoxy resin and the co-reactive chain extender.

Preferred lithium compounds useful as branching catalysts are lithium halides such as lithium chloride or lithium bromide; lithium acetate, lithium

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nitrate, butyl lithium, lithium perchlorate, lithium naphthenate, lithium-p-toluene sulfonate, lithium phenolate, lithium bisphenolate, lithium methanolate, lithium amide, lithium sulfide or lithium hydride.

5 Lithium and cesium hydroxide are also suitably employed as branching catalysts. Also, the halide salts of cesium and lithium which are formed by
10 reaction with the aliphatic halide present in the reaction mixture during the branching reactions are effective branching catalysts. The preferred lithium
15 compounds are lithium chloride and lithium phenolate, with lithium chloride being the most preferred lithium salt.

20 The lithium or cesium branching catalyst can be added prior to or subsequent to the advancement of the epoxy resin. The lithium or cesium salts are
25 preferably added only after advancement if the particular salt is soluble in the advanced epoxy resin. Lithium and cesium salts, which are insoluble
30 in the advanced reaction mixture but soluble in the reactant mixture, e.g., LiOH, are suitably added to the reaction mixture prior to advancement of the epoxy resin. The lithium or cesium compound is
35 employed in a catalytically effective amount. Advantageously, more than 0.1, preferably more than 1 and less than 100, preferably less than 30, ppm are
40 employed based on the amount by weight of the epoxy resin components in the branching reaction.

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Preferably, the advancement and/or branching reaction is conducted in the absence of a reaction diluent. In general, the branching reaction is 5 advantageously conducted at temperatures above 20°C, preferably above 140°C, and below 250°C, preferably below 200°C.

Upon obtaining the desired amounts of branching, the reaction is most effectively terminated by the addition of a material which acts to stop the 15 branching reaction. A particularly preferred method of preparation comprises branching an epoxy resin using a lithium compound as a branching catalyst and 20 there after terminating the branching reaction by adding a deactivating agent such as a strong acid, (i.e. an acid having pKa of less than 2.5 at 25°C), 25 e.g., inorganic acids such as phosphoric acid, sulfuric acid or sulfuric acid; inorganic acid esters; half esters and partial esters such as dimethylsulfate and monomethyl sulfate; inorganic 30 acid anhydrides such as phosphoric acid anhydrides (P_2O_5 or P_4O_{10}); strong organic acids, their esters and anhydrides, e.g., the alkyl and aralkyl sulfonic 35 or sulfenic acids such as p-toluene sulfonic acid anhydride. Of the foregoing compounds, those preferably employed as deactivators herein include 40 the alkyl, aryl and aralkyl sulfonic acids and the alkyl, aryl and aralkyl sulfonates. Most preferred are methyl-p-toluene sulfonate and p-toluene sulfonic acid. Preferably, the deactivator is added in an

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amount of at least 1 to less than 3 equivalents for each equivalent of the branching catalyst.

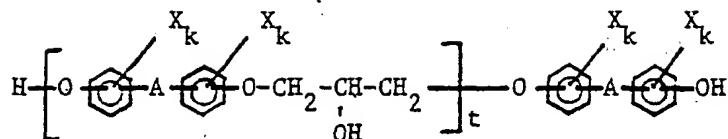
For the curing of the epoxy resins described
5 above, curing or cross-linking agents ("hardeners") well known in the art are useful. The compositions of the present invention contain solid curing agents,
10 for example, amines, acid anhydrides, boron trifluoride complexes, dicyandiamide, substituted dicyandiamides, polyester resins, and phenolic
15 hardeners.

Another class of curing agents well known in the art comprises prereacted adducts of epoxy resins with
20 amines or anhydrides or dicyandiamide or phenolic resins.

One particular class of phenolic hardeners
25 useful for the powder coating composition of the invention is the reaction product of A) an excess of a phenolic compound having on the average more than
30 one phenolic -OH group per molecule with B) an epoxy compound having on the average more than one 1,2-epoxy group per molecule.

35 The phenolic compound A) advantageously employed in preparing the phenolic hardener is a normally solid material and includes phenolic compounds
40 represented by the following general formulas III and IV:

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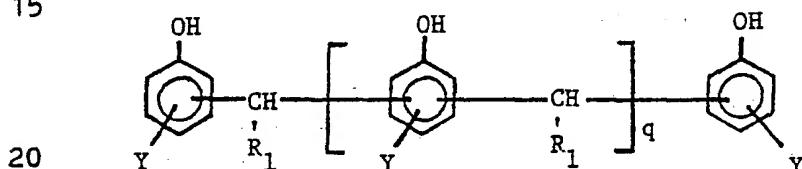


5

(III);

wherein A, and k are as defined in the description of
10 formula I and t has an average value of 0 to 5,
preferably from 0 to 2, and

15



(IV);

25 (commonly referred to as a novolac resin) wherein
each R₁ is individually hydrogen or an alkyl radical
having from 1 to 4 carbon atoms, each Y is an
independently hydrogen, chlorine, bromine or a lower
30 alkyl group of 1 to 6 carbon atoms and has an average
value from 0 to 10. Mixtures of different phenolic
compounds are also suitably employed herein.

35 Preferably, the phenolic compound A) employed
for preparing the phenolic hardener is a polyhydric
phenolic compound of the general structural formula
40 III wherein A is a divalent hydrocarbon radical
having from 1 to 8 carbon atoms, X in each occurrence
is hydrogen, and t is 0. Most preferred of the

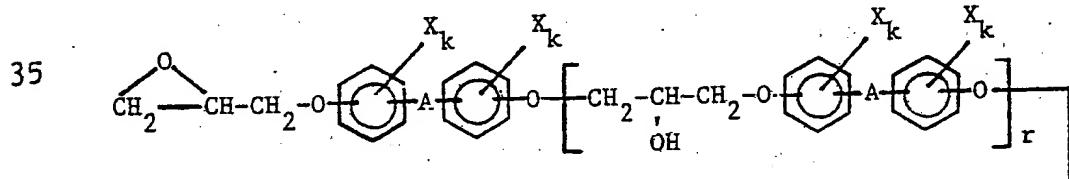
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polyhydric phenolic compound is 2,2-bis(4-hydroxyphenyl)propane, commonly referred to as bisphenol A.

5 In general, the epoxy compound B) used for preparing the phenolic hardener is saturated or unsaturated aliphatic, cycloaliphatic, aromatic or
 10 heterocyclic and can be substituted with one or more non-interfering substituents such as halogen atoms, groups containing phosphorous atoms, hydroxyl groups, alkyl and alkoxy radicals. The epoxy compound B) can
 15 be monomeric or polymeric.

Illustrative examples of epoxy compounds B)
 20 useful herein are described in The Handbook of Epoxy Resins by H. L. Lee and K. Neville, published in 1967 by McGraw-Hill, New York, in appendix 4-1, pages 4-35 through 4-56.

25 Epoxy compounds B) of particular interest in the practice of this embodiment include the polyglycidyl ethers of bisphenol compounds represented by the
 30 general structural formula:

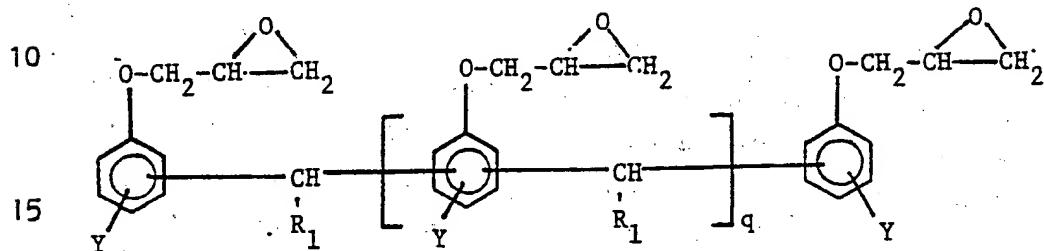


(V);

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wherein A, X and k are as defined above in formula I and r has an average value of 0 to 0.5; or

5 the polyglycidyl ethers of a novolac resin, i.e.
phenol aldehyde condensates of the formula:



20

(VI);

wherein R_1 , Y and q are defined as above with
reference to formula IV;

30 or polyglycidyl ethers of a polyglycol such as
diglycidyl ether of polypropylene glycol or the
polyglycidyl ethers of tris(phenol) methane.

Mixtures of several epoxy compounds are also suitably employed herein.

35

Preferred epoxy compounds B) are the poly-glycidyl ethers of bis-phenol compounds of formula (V) wherein each A is independently a divalent hydrocarbon group having from 1 to 6 carbon atoms, X in each occurrence is independently hydrogen or bromine and r has an average value of from 0 to 0.25,

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and also the polyglycidyl ethers of a novolac resin of formula VI wherein R₁ is hydrogen or methyl, each Y is hydrogen or methyl and q has an average value of from 0 to 3 and mixtures thereof. Most preferred as 5 an epoxy compound B) is the liquid diglycidyl ether of bisphenol A.

10 When preparing the phenolic hardeners, the phenolic compounds A) described above are employed in a stoichiometric excess when compared to the epoxy 15 compounds B) described above. Advantageously, at least 1.2 equivalents of the phenolic compound A) are employed for each equivalent of epoxy compound B).

20 Preferably, at least 1.5, more preferably at least 2, and preferably not more than 15, more preferably not more than 10, equivalents of the phenolic compound A) are employed per equivalent of epoxy compound B).

25 Most preferably, the phenolic compound A) is employed in an amount from 2 to 5 equivalents for each equivalent of epoxy compound B) employed.

30 The most preferred phenolic hardeners employed in the powder coating composition of the present invention are the reaction products of A) the

35 phenolic compound and B) the epoxy compound described above which have additionally been reacted with C) a compound containing at least one primary or secondary 40 amino group and at least one aliphatic hydroxyl group (hereafter "aliphatic hydroxyl containing amine").

This reaction product (hereafter "modified phenolic hardener") of A) the phenolic compound, B) the epoxy

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compound and C) the aliphatic hydroxyl containing amine has terminal aliphatic -OH groups and phenolic -OH groups.

5 By the term "aliphatic hydroxyl group" it is meant that the oxygen atom of the hydroxyl group is not attached directly to an aryl substituent. For 10 example, the hydroxyl group of phenol is not an aliphatic hydroxyl group whereas the hydroxyl group of benzyl alcohol is considered an aliphatic hydroxyl 15 group.

Representative examples of aliphatic hydroxyl containing amines are the monoamines having two 20 alkanol substituted groups (dialkanol amines) such as diethanol amine, dipropanol amine and ethanol propanol amine; monoamines having one alkanol 25 substituent such as ethanol amine and monoamines having one alkanol substituent and one other substituent group such as ethyl ethanol amine, methyl 30 ethanol amine and benzylethanol amine and polyamines such as N,N'-di(hydroxyethyl)ethylenediamine.

Preferred of the aliphatic -OH containing amines are the secondary monoamines. More preferably, the 35 aliphatic -OH containing amine is a dialkanol monoamine, with diethanolamine being most preferred.

In general, in preparing the above mentioned 40 modified phenolic hardener, the aliphatic -OH containing amine component C) is employed in an amount from 0.03 to 0.8, preferably from 0.08 to 0.4, equivalents per equivalent of epoxy compound B). An

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equivalent of the aliphatic hydroxyl containing amine C) as defined herein is determined by the number of hydrogen atoms attached directly to the nitrogen 5 atoms of the amine group which are capable of reacting with the epoxy compound. In other words, where X is the equivalent of B), generally 0.03 X to 0.8 X equivalents of C) are used.

10 When producing the modified phenolic hardener, a stoichiometric excess of the phenolic compound A) 15 when compared to the epoxy compound B) set forth above is employed. As set forth above, 1.2 to 15 equivalents of the phenolic compound A) are generally used per equivalent of epoxy compound B). However, in 20 determining the equivalents of phenolic compound A) and epoxy compound B) to be employed, it is necessary to take into consideration the fact that the 25 aliphatic -OH containing amine C) will react with the epoxy groups of the epoxy compound B) to reduce the epoxide functionality. Taking the equivalents of C) 30 into consideration, the equivalents of the epoxy compound B) not having reacted with C) are (X - 0.03) to (X - 0.8). Accordingly the equivalents of A) 35 generally employed is (1.2 to 15)·[(X - 0.03) to (X - 0.8)].

40 A particularly preferred modified phenolic hardener containing terminal aliphatic -OH groups and phenolic -OH groups is prepared using A) from 90 to 35 weight percent of bisphenol A, B) from 10 to 55 weight percent of the diglycidyl ether of bis-phenol

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A, and C) from 1 to 10 weight percent of the aliphatic hydroxyl containing amine, preferably diethanolamine.

5 The modified phenolic hardeners which are useful in the coating composition of the present invention are solids.

10 The phenolic hardeners and modified phenolic hardeners can be prepared by mixing the desired amounts of the phenolic compound A), the epoxy 15 compound B) and optionally the aliphatic hydroxyl containing amine C) and heating the mixture, generally to a temperature of 100 to 250°C.

20 When preparing the phenolic hardeners, a catalyst can be used for promoting the reaction of the epoxy groups with the phenolic groups. Such 25 catalysts are known in the art. The use of a catalyst, however, is generally not required, when the aliphatic hydroxyl containing amine C) which can 30 itself act as a catalyst for the reaction between the epoxy and the phenolic groups is present.

35 The described preferred powder coating compositions which contain the described solid epoxy resins and the described preferred (modified) phenolic hardeners exhibit good adhesion when applied 40 to a metal substrate, including a steel substrate. Although the powder coating composition of the present invention is particularly advantageous when applied to a steel substrate, it can also suitably be

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employed with other metallic substrates as well as substrates of other materials, including plastic or glass, which will withstand temperatures greater than 5 100°C.

Also a mixture of curing agents can be used. Generally, suitable amounts of curing agents are from 10 about 2 to 90, preferably from about 2 to 40 percent, based upon the total weight of the powder composition. For example, dicyandiamide or substituted 15 dicyandiamides are generally used in amounts of about 2 to about 10, preferably about 2 to about 5 percent by weight, based upon the total weight of the powder composition.

20 Phenolic hardeners are generally used in amounts of more than about 2, preferably more than about 10 25 and less than about 50, preferably less than about 40 percent by weight, based upon the total weight of the powder composition.

30 Linear or branched carboxyl-terminated solid polyester resins can be used as co-resins and as curing agents for the epoxy resins described above. 35 These polyester resins are generally used in amounts of more than about 20, preferably more than about 30, and less than about 80, preferably less than about 75 percent by weight, of the total powder composition.

40 Generally, the most preferred weight ratio between epoxy resin and curing agent comprised in the coating composition of the invention depends on a

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variety of factors, e.g., on the type of the epoxy resin and the curing agent, on the desired properties of the coating composition and on the type and amount of optional additives used.

In preparing a powder coating composition of the invention the solid epoxy resin described herein and the solid curing agent for the epoxy resin are preferably employed in amounts such that the powder coating composition contains from 45 to 95, preferably from 60 to 90, weight percent of the epoxy resin and from 55 to 5, preferably from 40 to 10, weight percent of the curing agent, said weight percents being based on the total weight of the solid curing agent and solid epoxy resin employed.

In general, the equivalents ratio between epoxy groups in the resin and reactive groups in the curing agent is from 2:1 to 1:2, preferably from 1.5:1 to 1:1.2.

The most preferred molar ratio between epoxy groups and active hydrogen groups for the specific type and use of the coating composition can be determined by those ordinary skilled in the art.

Optionally, accelerators or catalysts for promoting the reaction between the epoxy resin and the curing agent are used in preparing the powder coating compositions. Suitable accelerators include, for example, quaternary ammonium compounds, quaternary phosphonium compounds, oxazines,

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oxazolines, imidazoles and imidazolines which are well known in the art. Catalysts are preferably employed in an amount of more than about 0.01 5 percent, more preferably more than about 0.05 percent; and preferably less than about 1.0 percent, more preferably less than about 0.8 percent by weight, based upon the total weight of the powder 10 coating composition. In the practice of the present invention the catalysts or accelerators are often premixed with the curing agent or with the epoxy 15 resin.

Optionally, the powder coating composition may contain several adjuncts, e.g., flow control agents, 20 additives for improving the handling properties, pigments or fillers. These adjuncts are well known in the art.

25 For example, if desired, flow control agents can be added to the powder coating composition of this invention, preferably in amounts of 0.01 to 1.0 30 weight percent, based upon the total weight of the powder coating composition. Typical flow control agents are polyacrylates, such as poly-2-ethylhexyl 35 acrylate, finely divided ethyl cellulose, and siloxanes, such as dimethyl polysiloxanes or methyl phenyl polysiloxanes. Benzoin can also be used in 40 order to improve the flow of the coating.

To improve the handling properties of the powder coating composition and to prevent caking, finely divided silica, generally in the amounts of more than

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0.05 percent, preferably more than 0.1 percent and less than 5.0 percent, preferably less than 3.0 percent, by weight of the powder coating composition can be added. The silica can be blended with the 5 epoxy resin with the curing agent and/or the catalyst.

10. The powder coating composition can contain pigments. Any of the conventional inorganic or organic pigments, filler pigments, or dyes can be used. Examples of the great variety of usable 15 pigments include: metallic oxides, such as titanium dioxide, zinc oxide, and iron oxide; metallic flakes such as aluminum flake; metallic powders; metal 20 hydroxides; sulfides; sulfates; carbonates; carbon black; silica; talc; china clay; and other extender pigments. Preferably, the powder coating composition 25 contains more than about 5 percent, most preferably more than about 10 percent, and less than about 60 percent, most preferably less than about 40 percent, 30 by weight of the pigment.

The application of the powder coating composition to a substrate can be done by spraying or 35 dipping the substrate into a fluidized powder coating composition.

Generally, electrostatic spraying equipment is 40 used in which a voltage of about 20 to about 100 kilovolts is applied to the spray gun. The composition can be applied to a cold or to a preheated substrate in one pass or several passes to

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provide variable coating thickness, after cure, of preferably 0.01 to 0.70 mm. For protective applications like pipe coatings, the coating thickness after 5 curing is most preferably from 0.15 to 0.7 mm. For standard decorative applications a coating thickness of 0.04 to 0.10 mm is particularly preferred.

10 The powder coating composition can be advantageously applied directly to metals such as aluminum or steel. The coating composition can also 15 be applied to a suitably treated or primed metal substrate. The composition can be sprayed directly on galvanized, phosphatized or chromated steel or chromated aluminium to form a durable coating.

20 After the application of the powder, the coated article is preferably subjected to a temperature of 25 100°C to 350°C, most preferably of 140°C to 300°C, for about 1 to 30 minutes to fuse and to cure the powder particles into a substantially continuous uniform 30 coating.

When pipes are coated, the coating is generally applied to preheated pipes which preferably have a 35 temperature of between about 150°C and about 300°C. Accordingly, the melt-viscosity of the composition should be high enough to prevent sagging of the sprayed composition. A small amount of additives 40 which raise the melt-viscosity of the composition, e.g., a small amount of a higher molecular weight (3000 or more) epoxy resin can optionally be added to obtain the desired properties of the powder

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composition used for coating pipes. The residual heat of the pipe is generally sufficient to fully cure the coating.

5 Typical applications for decorative epoxy coatings include, for example, office furniture, bicycle frames, hot-water radiators, toys and tools, 10 road signs and other metallic substrates. Protective epoxy powder compositions are applied, for example, to pipes, automotive chassis, farm machinery, fences 15 and tanks.

The following examples illustrate the invention and should not be construed to limit the scope. In 20 the examples, all parts and percentages are by weight unless otherwise indicated.

25 A) Preparation of a multifunctional epoxy resin A

To a suitably sized reaction vessel equipped 30 with a temperature control means, stirring device and nitrogen sparger, were added 800 parts of a mixture containing 606.1 parts of a diglycidyl ether of 35 bisphenol A (epoxy equivalent weight (EEW) of 180) and 193.9 parts of bisphenol A. The reaction vessel was then heated to 95°C. When the contents of the 40 reaction vessel obtained this temperature, 0.2 part of a 70 percent solution of ethyltriphenyl phosphonium acetate advancement catalyst in methanol and 0.16 part of a 10 percent solution of LiOH

branching catalyst in water were added to the reaction vessel. The active amount of advancement catalyst was 175 parts per million parts of the epoxy resin. The active amount of the LiOH branching catalyst was 20 parts per million parts of the epoxy resin. The resulting reaction mixture which contained both the advancement and branching catalyst was heated to 150°C. At this temperature, the reaction mixture was found to exotherm, with the exotherm temperature being between 180 and 200°C.

15 The temperature of the reaction mixture was maintained at 180°C after the exotherm has been passed.

20 When the EEW reached the desired EEW of 590, which occurred about 2.25 hours after the initial exotherm, 0.16 part of methyl-p-toluene sulfonate was added, in one shot, to the reaction mixture. The reaction mixture was maintained at 180°C for thirty minutes to allow the deactivator to be homogeneously mixed throughout the reaction mixture and sufficiently deactivate the catalyst and to terminate the branching chain propagation. Subsequent to this treatment, the reaction mixture was found to be stabilized and was flaked using conventional techniques.

40 The resulting branched epoxy resin has an average epoxide functionality of about 2.6, a melt viscosity, at 150°C, of 27.6 poise, a softening point of 93.1°C and glass transition temperature of 48°C.

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B) Preparation of a preferred phenolic hardener B

5 To a suitably sized glass vessel equipped with stirrer, heating mantle, temperature control means and nitrogen purge, were charged 37.9 parts of a
10 commercially available diglycidyl ether of bisphenol A (0.203 equivalent), 53.1 parts of bisphenol A (0.465 equivalent) and 5 parts of diethanol amine
15 (0.048 equivalent). This reaction mixture was heated to 150°C and allowed to exotherm. The reaction was allowed to proceed for an additional 90 minutes to
20 assure that the reaction product contained essentially no residual epoxy groups. At this time, the reaction mixture was cooled to less than 140°C. Subsequently, 2 parts of 2-methylimidazole and 2
25 parts of a flow control agent were mixed into the reaction product. It was then cooled to room temperature and flaked.

30

Preparation of the powder coating compositions

35 Example 1

30.0 parts of the multifunctional epoxy resin A
40 prepared as described above; 36.0 parts of a polyester resin which is employed as a curing agent and which is commercially available from SCADO Netherlands under the designation Uralac P2127; 32.5

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parts of a titanium dioxide pigment; 0.5 part benzoin; and 1.0 part of a polyacrylate flow control agent which is commercially available from Worlee-
5 Chemie GmbH under the description Resiflow PV 5 were mixed, the mixture was extruded on a Buss PR46 type extruder at 120°C and the extrudate was ground and sieved to a particle size of less than 120 microns.
10 Then the formulation was electrostatically sprayed at a voltage of 40 to 100 kilovolts, onto 0.6 mm thick, degreased, unheated steel panels of the dimensions 15
15 cm by 7 cm and cured at 180°C.

20 Example 2

A powder coating composition was prepared in the same manner as in Example 1 except that 15.5 parts of
25 the multifunctional epoxy resin A and 50.5 parts of a polyester resin which is commercially available from SCADO Netherlands under the designation Uralac P 2450
30 were employed.

35 Example 3

43.0 parts of the multifunctional epoxy resins A prepared as described above; 17.0 parts of a phenolic
40 curing agent, commercially available as D.E.H. (Trademark of The Dow Chemical Company) 81 curing agent; and 40.0 parts of a titanium dioxide pigment were mixed and the mixture was extruded on a Buss PR

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46 type extruder at 86°C. The treatment of the extrudate and the application of the coating formulation to the substrate was the same as in
5 Example 1.

In Table I some physical and chemical properties of the coatings prepared from the coating
10 compositions of Examples 1 to 3 are listed.

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TABLE I

	Examples		
	1	2	3
Gel time (sec.) at 180°C	105	145	47
Stoving temperature (°C)	180	180	180
Stoving time (min.)	25	25	4
Thickness (microns)	55	60	55
Flow	good	good	fair
Gloss (60° angle)	87%	76%	good
Impact front/reverse inch-lbs (m.kg)	160/160 (1.84/1.84)	<60 (<0.69)	160/160 (1.84/1.84)
Erichsen flexibility (mm)	10.7	11.4	9.5
Adhesion	v. good	v. good	fair
Acetone rubs	18	2	10

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The gel time is measured according to DIN 55990-8. The properties of the cured coating are measured as follows:

5

Gloss (60° angle) DIN 67530

Front/reverse impact ASTM D-2794-69

10

Erichsen flexibility DIN 53156

10

Adhesion DIN 53151

15 The acetone rubs test measures solvent resistance. For this test a wad of cotton-wool soaked with acetone is used. The wad of cotton-wool is passed over the surface of the coating. The 20 number of passes required until the coating turns matt or turbid is counted.

25 Coatings containing epoxy resin A in an amount of more than 25 percent by weight, based on the total weight of the coating composition are more solvent 30 resistant and generally also more resistant to impact than those containing less than 20 percent by weight of epoxy resin A. Therefore, the powder coating compositions of the present invention most preferably contain more than 25 percent by weight of the solid 35 multifunctional epoxy resin having an average epoxide functionality per molecule of greater than two. Examples 1 to 3 illustrate that the coating 40 compositions are useful for decorative applications.

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Example 4

49.0 parts of the multifunctional epoxy resin A
5 prepared as described above; 10.5 parts D.E.H.
(Trademark of The Dow Chemical Company) 81 curing
agent; 10.5 parts D.E.H. (Trademark of The Dow
10 Chemical Company) 82 curing agent; 12.0 parts of a
red iron oxide pigment; 15.0 parts of a barium
sulphate filler; and 3.0 parts of a finely divided
silica which is commercially available from Degussa
15 under the designation Aerosil 972-R were mixed, the
mixture was extruded on a Buss PR 46 type extruder at
85°C ± 2°C and the extrudate was flaked, ground and
20 sieved to a particle size of less than 120 microns.
Then the formulation was electrostatically sprayed at
a voltage of 40-100 kilovolts onto 6 mm thick, blast
25 cleaned steel panels preheated to 235°C of the
dimensions 15 cm by 7 cm.

Example 5

30 A powder coating composition was prepared and
applied to steel panels in the same manner as in
Example 4 except that 50.0 parts of the multi-
35 functional epoxy resin A, 10.0 parts D.E.H.
(Trademark of The Dow Chemical Company) 81 phenolic
curing agent and 10.0 parts D.E.H. (Trademark of The
40 Dow Chemical Company) 82 phenolic curing agent were
employed instead of the amounts of resin and
hardeners in Example 4.

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Example 6

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50.0 parts of the multifunctional epoxy resin A; and 20.0 parts of the phenolic curing agent B), both prepared as described above; 12.0 parts of a red iron oxide pigment; 15.0 parts of a barium sulphate filler; and 3.0 parts of a finely divided silica which is commercially available from Degussa under the designation Aerosil 972-R were mixed. The extrusion of the mixture, the preparation and application of the powder coating composition took place as in Example 4.

20

25 Comparative Example

42.5 parts and 6.5 parts of epoxy resins which are commercially available as D.E.R. (Trademark of 30 The Dow Chemical Company) 642U epoxy resin and D.E.R. (Trademark of The Dow Chemical Company) 672U epoxy resin respectively, and which are both novolac modified solid reaction products of epichloro-hydrin 35 and bisphenol A, and the same amounts and types of hardeners and additional adjuncts as employed in Example 4 were mixed. The mixture was treated and 40 applied to steel panels as in Example 4. The mixture of the comparative Example is one of the best presently commercially available.

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In Table II, some physical and chemical properties of the coatings prepared from the coating compositions of Examples 4 to 6 and the comparative 5 example are listed.

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TABLE II

	Examples			Comparative Example
	4	5	6	
Thickness (microns)	350-400	350-400	350-400	350-400
Gel time (sec.) at 180°C	36	48	40	43
Application temp. (°C) (substrate)	235	235	235	235
Post cure (min.) at 235°C	3	3	3	3
Impact resistance inch·pounds (m·kg)	76 (0.87)	32 (0.37)	44 (0.51)	40 (0.46)
Flexibility	>110°	>110°	>110°	80°
Cathodic disbondment 28 days at room temp. (mm)	8.3	3.5	3.5	6.2
7 days at 50°C (mm)	5.8	4.5	3.3	6.7

The gel time and the impact resistance were measured as in Examples 1 to 3.

5 The flexibility was measured by bending the steel plate over a mandrel of 30 mm. The angles listed in Table II are the maximal angles of bend at 10 which the coating is still intact.

15 The cathodic disbondment was measured by drilling a hole of 2.5 mm diameter through the coating to the steel panel, putting the panel into a 3 weight percent NaCl solution and applying a potential of 6 volts.

20 Examples 4 and 5 illustrate that by varying the ratio between epoxy resin and hardener the properties of the coating can be adjusted to give the desired 25 balance of properties for the specific application. The coating composition of Example 6 provides an excellent balance of impact resistance and resistance 30 to cathodic disbondment.

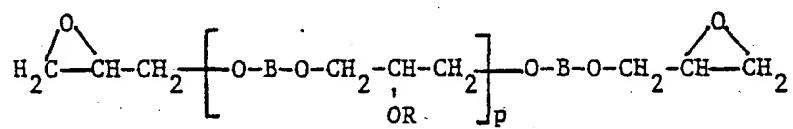
35 The comparative example also provides good impact resistance and resistance to cathodic disbondment. However, the flexibility of the coatings of Example 4 to 6 is considerably better than of the comparative example.

40 The powder coatings of Example 4 to 6 are useful as protective coatings, e.g. for the protection of pipes.

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1. A powder coating composition comprising a solid epoxy resin and a solid curing agent for the epoxy resin characterised in that the solid epoxy resin is a solid, multifunctional polyglycidyl ether of a bisphenol compound or a solid, multifunctional polyglycidyl ether of a polyglycol advanced in 5 molecular weight with a bisphenol compound of formula I

10



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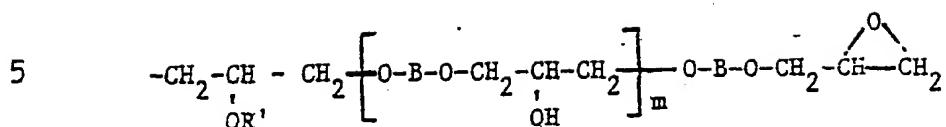
(I);

20

wherein R is independently, each occurrence, hydrogen or a group of formula II

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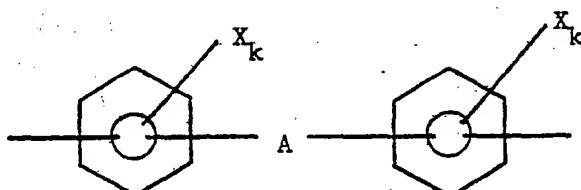


10

(II);

R' has the meaning of R; each B is independently an
15 aliphatic alkyl radical, a radical of formula

20



25

(VII);

30 or a polyglycol radical of a number average molecular weight from 100 to 4000; provided that at least a part of the radicals B are radicals of formula VII;

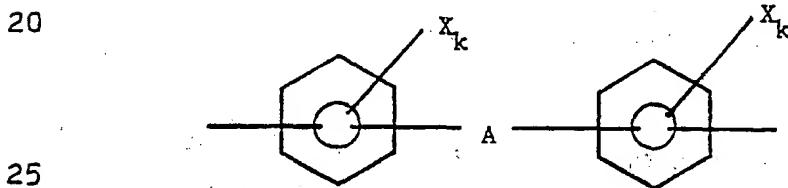
35 each A is independently, each occurrence, a divalent hydro-carbon group having from 1 to 8 carbon atoms, -CO-, -O-, -S-, -S-S-, -S(O)₂-, -S(O)- or a covalent
40 bond;

X is independently, each occurrence, hydrogen, halogen or an alkyl group of 1 to 4 carbon atoms;

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5 p has an average value greater than 0 and up to 20, m
has an average value of 0 up to 20, and k is a
positive number from 1 to 4; provided that the
10 formula I.

15 2. The composition of Claim 1 wherein the
epoxy resin is a multifunctional polyglycidyl ether
of formula I wherein at least a part of the radicals
B are represented by formula



(VII);

30 30 wherein A is independently, each occurrence, a
divalent hydrocarbon group having from 1 to 6 carbon
atoms; X is independently, each occurrence, hydrogen,
bromine or chlorine, k is a positive number from 1 to
35 4 and the epoxy resin has an average epoxide
functionality per molecule of 2.1 to 5.0.

40 40 3. The composition of Claim 2 wherein the
epoxy resin is a multifunctional polyglycidyl ether
of formula I wherein, in the radicals B, each A is a
2-propylidene radical and X in each occurrence is

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hydrogen and the epoxy resin has an average epoxide functionality of 2.3 to 3.5.

4. The composition of any of Claims 1 to 3
5 wherein the solid multifunctional epoxy resin is an
epoxy resin which has been branched in the presence
of an alkali compound, preferably a lithium or cesium
10 compound.

5. The composition of any of Claims 1 to 4
wherein the solid curing agent for the epoxy resin is
15 the reaction product of A) an excess of a phenolic
compound having on the average more than one phenolic
-OH group per molecule with B) an epoxy compound
20 having on the average more than one 1,2-epoxy group
per molecule.

6. The composition of any of Claims 1 to 4
25 wherein the solid curing agent for the epoxy resin is
the reaction product of A) a phenolic compound having
on the average more than one phenolic -OH group, B)
30 an epoxy compound having on the average more than one
1,2-epoxy group and C) a compound containing at least
one primary or secondary amino group and at least one
35 aliphatic hydroxyl group, said reaction product
having terminal aliphatic -OH groups and phenolic -OH
groups.

40 7. The composition of Claim 6 wherein the
solid curing agent is prepared by reacting with each
equivalent of the epoxy compound from 0.03 to 0.8
equivalents of a compound C) containing at least one

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primary or secondary amino group and at least one aliphatic hydroxyl group, and by using at least 1.2 equivalents, of a phenolic compound A), for each 5 equivalent of the epoxy compound B) being in excess of the stoichiometric amount required for reacting with amino hydrogens of the compound C).

10. 8. The composition of Claim 6 or 7 wherein the solid curing agent is the reaction product of A) from 90 to 35 weight percent of bisphenol A, B) from 15 10 to 55 weight percent of the diglycidyl ether of bisphenol A, and C) from 1 to 10 weight percent of the compound containing at least one primary or secondary amino group and at least one aliphatic 20 hydroxyl group, preferably diethanol amine.

9. Use of the powder coating composition of 25 any of Claims 1 to 8 for coating a substrate.

10. A substrate having on at least one surface thereof the cured coating composition of any 30 of Claims 1 to 8.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/02035

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4) : C08G 59/06, 59/32, 81/00
US CL 525/526

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
U.S.	525/484, 526, 934

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁶
A	US,A, 4,251,426 (MCCLURE) 17 FEBRUARY 1981.	
A	US,A, 4,526,940 (SEYMOUR) 02 JULY 1985.	
A, P	US,A, 4,552,814 (CAVITT) 12 NOVEMBER 1985.	

* Special categories of cited documents: ¹⁵

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁸

16 JANUARY 1987

Date of Mailing of this International Search Report ¹⁹

02 FEB 1987

International Searching Authority ¹

ISA/US

Signature of Authorized Officer ²⁰

E. Nielsen
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